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To cite this article: S P Arkhipov *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **734** 012024

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Rhenium behavior in the $\text{KF-KBF}_4\text{-B}_2\text{O}_3\text{-KReO}_4$ melt

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Abstract. The present paper is devoted to the study of the electrolyte temperature influence on the cathode process of rhenium reduction on the glassy carbon anode by the cyclic voltammetry method. Experimental dependencies, which characterize the influence of the KReO_4 addition on the $\text{KF-KBF}_4\text{-B}_2\text{O}_3$ system liquidus temperature, were built according to the obtained data on the thermal analysis. It was found that rhenium reduction at lower electrolyte temperatures requires higher values of cathode overpotential.

1. Introduction

Currently, selection of materials, which are high corrosion- and mechanically resistant at high temperatures, is an important task of material science. This problem is especially vital for the aerospace industry, because operational conditions in this field include temperatures of 1500 °C, oxidation media and pressure overfalls.

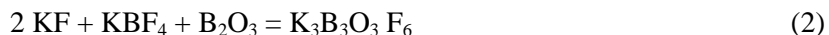
Rhenium is a promising long-wearing material for jet engines, combustion chambers and turbine blades, because of its unique physical-chemical properties, such as high melting (3170 °C) and boiling (5600 °C) temperatures, as well as corrosion resistance in humid media.

Molten salt electrolysis is the most advanced technique of rhenium coatings formation. The possibility to use non-organic rhenium compounds at the material component preparation is the main advantage of the electrochemical technique [1, 2]. Fluoride melts of the $\text{KF-KBF}_4\text{-B}_2\text{O}_3\text{-KReO}_4$ type are of the greatest interest as opposed to the chloride electrolytes [3, 4] the rhenium concentration in their composition may be controlled by the potassium perrhenate additions [5].

To obtain high quality rhenium deposits it is vital to select optimal electrolysis parameters. The process temperature is one of the basic parameters, which is directly associated with the liquidus temperature.

There is a lack of data on the $\text{KF-KBF}_4\text{-B}_2\text{O}_3$ system liquidus temperature. However, there is information provided by A. Kataev, O. Tkacheva *et al.* [6] on the influence of the boron oxide addition on the electrolyte liquidus temperature in the KF-AlF_3 and KF-NaF-AlF_3 melts.





The oxy-fluoroborate compound, which was obtained according to reaction (1) was used as a side electrolyte for rhenium coating formation in air [5]. The present work is aimed at the study of the potassium perrhenate on the liquid temperature of the $\text{K}_2\text{B}_2\text{OF}_6$ compound, as well as at the study of the influence of the electrolysis temperature regime on the cathode process of rhenium reduction on the glassy carbon electrode.

2. Experimental part

The melts used in the present study were prepared from individual salts. The electrolytes were prepared from chemically pure reagents: $\text{KF} \cdot \text{HF}$ (Vecton Ltd, St. Petersburg, RF). Boron-containing KBF_4 , B_2O_3 and rhenium-containing KReO_4 compounds were supplied by the Reakhim Company (Moscow, RF). The powder of potassium perrhenate was preliminary dried in a glassy carbon container at 150 °C for 3 hours in air. Potassium tetrafluoroborate was dried at 200 °C for 2 hours. B_2O_3 was remelted in vacuum and then it was used for the melts preparation in the reground form.

The melts were prepared before each experiment in a glassy carbon container. A mixture of the following composition KF (37.28 wt. %)- KBF_4 (40.39 wt. %)- B_2O_3 (22.33 wt. %) was added into the container. Then it was heated to 773 K and the mixture was exposed in a molten state for 4 hours. The HF complete removal was determined by the analysis of the evaporation by a litmus solution.

The liquidus temperature was measured by the thermal analysis method. The cell was put into a glassy carbon glass with the melt under study. The sample weight of pure $\text{KF-KBF}_4\text{-B}_2\text{O}_3$ without potassium perrhenate addition was 160 g. 1 wt. % of KReO_4 was added through a quartz tube, which was lowered to the melt surface through a special opening in a fluoroplastic lid. The temperature changes were recorded by an S-type thermocouple (Pt - 10% Rh/Pt). The temperature measurements were recorded 1 time per second by an APPA 109N multimeter. At the heating temperature of 573 K the cell was vacuumed and then it was filled with argon and heated to the melting point. The above mentioned procedure was repeated after each perrhenate addition. The liquidus temperatures were measured under excess inert gas (Ar) pressure.

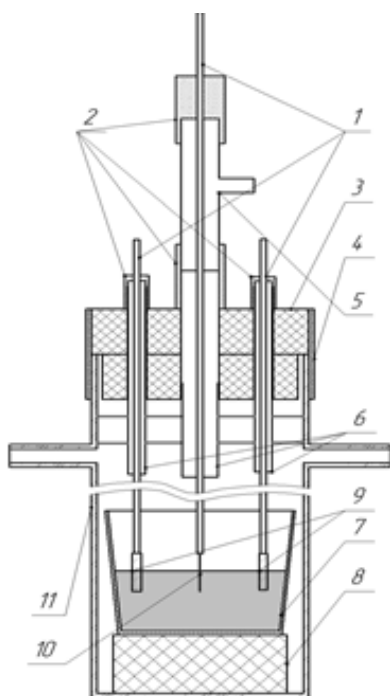


Figure 1. Scheme of the electrochemical cell: 1 – current leads; 2 – rubber seals; 3 – fluoroplastic cover; 4 – sealing ring; 5 – adaptor (transitional sluice); 6 – protective covers; 7 – glassy carbon container with melt; 8 – graphite support; 9 – Re electrodes; 10 – glassy carbon working electrode.

The study of the electrolyte temperature influence on the rhenium reduction cathode process from the melt was performed by the cyclic voltammetry method in a three-electrode hermetic quartz cell (figure 1) at 773 K in high purity dehydrated argon (99,999%) supplied by the Uralcriogas Company (Ekaterinburg, RF). The temperature was controlled by a Pt-Pt/Rh thermocouple. Rhenium rods (99,986 wt. % of Re), made of a pressed Re powder, were used as reference and counter electrodes. A working glassy carbon electrode (SU-2000, 99.999 %) supplied by Uralmetalgrazit (Chelyabinsk, RF) was washed by distilled water and ethanol and was dried under vacuum. A typical geometric surface area of the carbon glassy plates varied from 1.3 cm² to 2.5 cm².

The rhenium concentration in the KF-KBF₄-B₂O₃-KReO₄ electrolyte was 0.88 wt% ($7.77 \cdot 10^{-5}$ mol·cm⁻³, $4.68 \cdot 10^{19}$ cm⁻³).

Cyclic voltammograms were recorded using a galvanostate/potentiostate AUTOLAB PGStat 302N with Nova 2.0 software. The electrodes were exposed for 30 minute in the KF-KBF₄-B₂O₃-KReO₄ melt until the electrodes potentials equilibrium was reached before the measurements were performed. The electrochemical cell resistance was measured by the impedance spectroscopy method and it was balanced by AUTOLAB PGStat 302N.

3. Results and discussion

Figure 2 illustrates the liquidus temperature, which was obtained in the KF-KBF₄-B₂O₃-KReO₄ system. The KReO₄ concentration varied from 0 to 6 wt. %. The liquidus temperature of the electrolyte without potassium perrhenate additions was found to be 410 °C. The liquidus temperature of the system under study changed insignificantly at the KReO₄ addition, the greatest temperature growth was observed at the increase in potassium perrhenate concentration reaching 2 wt. %. The further growth of the KReO₄ concentration did not result in any significant changes in the melt liquidus temperature.

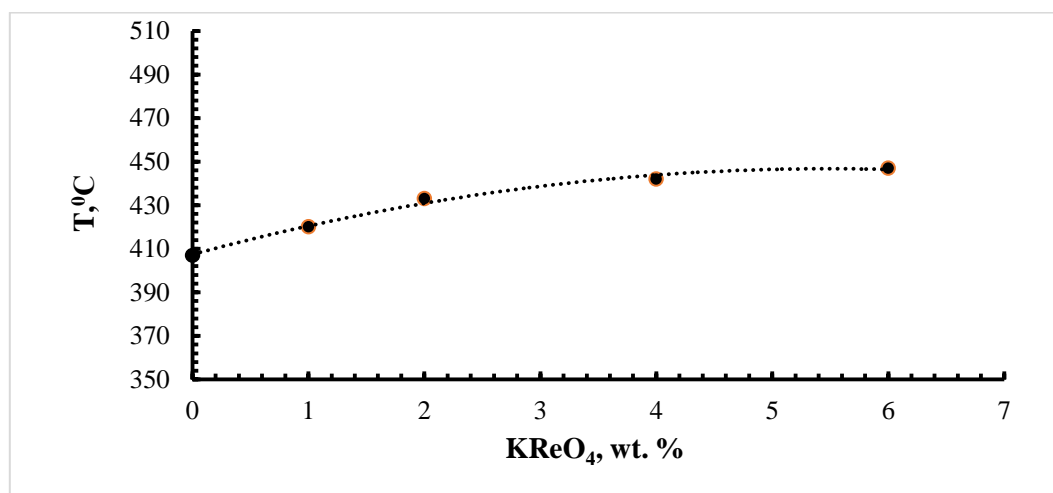


Figure 2. Influence of KReO₄ on the liquidus temperature of the KF-KBF₄-B₂O₃ system.

Figure 3 presents typical cyclic voltammograms obtained at the temperatures of 450 °C, 470 °C, 500 °C and the potential scanning rate of 0.4 V/s.

At the direct potential scanning only one peak corresponding to the rhenium reduction process was recorded on the curves 1, 2 and 3 in the cathode region at the electrolyte temperatures equal to 500 °C, 470 °C, 450 °C, respectively. Then the current decrease was observed on all curves. After the potential reverse ($\eta = 0.9$ V) a modified nucleation loop formed at the cross of the branches of direct and reverse scanning. The loop formation was caused by the changes in the cathode state during the scanning [7]. At the direct scanning the rhenium deposition started at the inert glassy carbon substrate,

but at the reverse scanning (before the transfer to the anode region) the rhenium electrocrystallization proceeded on the rhenium substrate (on the formed rhenium layer). This resulted in the shift of the potential to the anode region.

The results of the cyclic voltammetry studies elucidate that the rhenium cathode reduction at the lower electrolyte temperatures require more negative values of the overpotential.

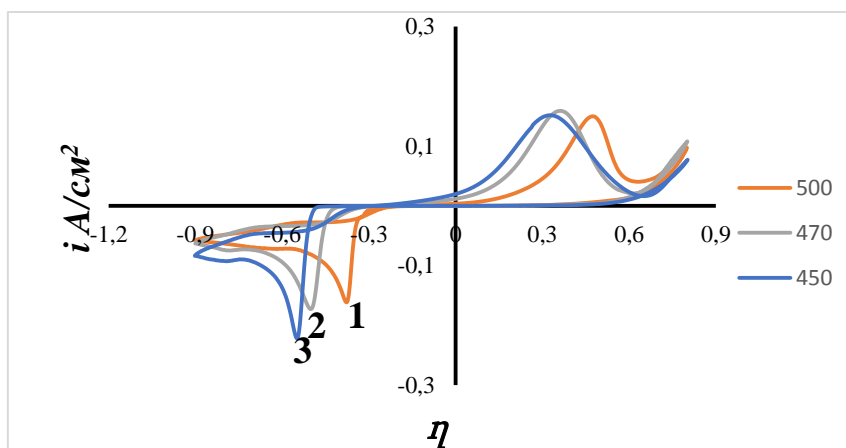


Figure 3. Cyclic voltammograms on the glassy carbon cathode in $\text{KF-KBF}_4\text{-B}_2\text{O}_3\text{-KReO}_4$ (0.88 wt% Re): 1 – 500 °C; 2 – 470 °C; 3 – 450 °C.

At the electrolyte temperature of 500 °C the peak corresponding to the rhenium reduction reaction is observed at $\eta = -0.3$ V, whereas at the temperature of 450 °C the rhenium reduction peak shifts greatly to the cathode region ($\eta = -0.6$ V). This may be caused by diffusion obstacles, associated with the transport of the reacting substance to the electrode surface, because of a relatively small rhenium concentration in the electrolyte.

4. Conclusions

The liquidus temperature of the $\text{KF-KBF}_4\text{-B}_2\text{O}_3$ system has been measured for the first time and it was found to be equal to 410 °C. The dependence of the $\text{KF-KBF}_4\text{-B}_2\text{O}_3$ liquidus temperature on the KReO_4 concentration was obtained. The influence of the electrolyte temperature on the rhenium cathode reduction on glassy carbon was studied by the cyclic voltammetry method.

Acknowledgements

The study was carried out with financial support of the Ministry of Education and Science of the Russian Federation within the frames of the Federal Target Program (the agreement number 14.578.21.0238, identification number RFMEFI57817X0238).

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